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CALCULATION OF EINSTEIN A COEFFICIENTS AND OSCILLATOR STRENGTHS FOR THE $\tilde{A}^2A_1$ - $\tilde{X}^2B_1$ TRANSITION OF NH_2

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The (NH_2) radical plays an important role in the decomposition chemistry of solid propellants, in particular nitramines. Additives which produce large amounts of NH_2 are also known to have burn rate acceleration effects on HMX based propellants, probably due to the reduction of NO by NH_2. We believe that these or similar additives may also produce important ignition enhancement effects and are planning studies in this area. In order to spectroscopically probe NH_2 in these studies, the strength of individual rovibronic transitions in the molecule's best known electronic transition, ($\tilde{A}^2A_1$) - ($\tilde{X}^2B_1$), must be known. Until recently, however, such information was available for only two lines and these were not precisely known. Recently, a method was presented (see References 2 and 3) whereby Einstein coefficients and oscillator strengths may be calculated for the individual lines. The calculation is straightforward, but not readily transparent to the uninitiated. We therefore promised in Reference 3 to make this monograph, which provides example calculations, available. Methods of identifying transitions involving perturbed levels, for

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which the calculation may not work well, are first discussed. Then an example calculation of a radiative lifetime for a vibrational level in the A state and calculations of the Einstein coefficients and oscillator strengths for two rovibrational lines are given. (AW)

TABLE OF CONTENTS

I. INTRODUCTION

The calculation of Einstein coefficients and oscillator strengths for most diatomic molecule transitions is a straightforward and relatively simple exercise (with the assumption that the electronic transition moment is constant as a function of internuclear distance). Franck-Condon factors (FCFs) and rotational linestrength factors (HLFs, for Honl-London factors) may be readily interpretted and combined to obtain the desired Einstein coefficients in a simple, easy to understand fashion. The FCFs and even the HLFs are frequently available in the literature since they are easily calculated using well-known procedures. This situation is, however, not the case for polyatomic molecules, especially in the case of asymmetric rotors. The calculation of vibrational intensity factors is not at all well worked out for these cases. For one particular case, that of NH_2 which is a radical of particular importance in combustion systems, recent work by Jungen, Hallin, and Merer[1] (JHM II) has resulted in vibronic transition moments (VTMs). (It is important to note that these are not FCFs because the integral involved in their calculation includes the electronic transition moment and its dependence on the bending vibration). We have shown in recent work[2,3] how these may be combined with data from the literature and HLFs calculated by a straightforward method to obtain Einstein coefficients and oscillator strengths of individual rovibronic transitions of NH_2. The calculation while being straightforward is, however, not readily transparent to the unintiated. Most users of this technique would find that it takes several days, perhaps even weeks, to correctly understand and apply the tables of JHM because so few data of this type are currently available. We therefore promised in Reference 3 to make this monograph, which explains the calculation in nauseating detail, available to interested parties simply by writing us. In addition, a computer program, suitable for use for calculating the HLFs for NH_2 or any other asymmetric rotor transition which may be approximated to be a singlet - singlet transition, is also available. The program is supplied on 5 1/4 inch floppy diskettes, compiled for IBM PCs (and compatibles).*

A short description of how the HLFs are calculated by the program is given here. (This information also appears on a documentation file on the program diskette.) Theory of the asymmetric rotor Hamiltonian which is used was derived by Watson.[4] The specific functional form of the Hamiltonian, written for either a prolate or oblate symmetric top basis set, is given by Camy-Peret and Flaud.[5] The Hamiltonian matrix may be diagonalized directly in the symmetric top basis. However, to make the computations simpler, the so-called Wang transformation[6] is first applied to the matrix; this results in block diagonalization of the matrix. (For a good introductory level discussion of the Wang transformation and its application to assymetric rotors, see Reference 7.) Diagonalization of this matrix then results in eigenvectors (wavefunction representations) of the asymmetric rotor states in

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*We have recently learned that another program is also available for calculation of intensities and positions of lines for asymmetric rotor transitions. See F.W. Birss and D.A. Ramsay, "Computer Assistance in the Analysis of Molecular Spectra. I. Rotational Structure of High Resolution Singlet-Singlet Bands," Computer Physics Communications, Vol. 38, p. 83, 1984.

the Wang-transformed basis set. These eigenvectors are then transformed back to the symmetric rotor basis set. Combination of the appropriate eigenvector pairs (written in the symmetric basis set) for a given transition with the direction cosine matrix elements (also written for the symmetric basis set) of Cross, Hainer and King[8] then yields the HLFs.

This monograph will first discuss how to identify transitions involving perturbed levels, in which case our method of calculating Einstein coefficients may not work well. Then we present example calculations of (1) the lifetime of an $\tilde{A}$ state vibrational level and (2) the Einstein coefficient and oscillator strength for two of the $\tilde{A}$-$\tilde{X}$ rovibronic transitions of NH_2. The first example will be the calculation of Einstein vibrational band coefficients for the emissions from the $(0,11,0)\Sigma$ level and their use to calculate the lifetime of this level. The latter examples will be calculations of the Einstein A coefficients and oscillator strengths for the $^{P}Q_{1},_{N}{}^{7}$ transition in the $(0,9,0)\Sigma - (0,0,0)$ band and the $^{R}Q_{0},_{N}{}^{4}$ transition in the $(0,12,0)\Pi - (0,0,0)$ band.

II. IDENTIFYING PERTURBED LEVELS

The method of calculation of the Einstein coefficients and oscillator strengths for NH_2 is discussed in Section II of Reference 3. The user of our method should be aware of the several caveats mentioned there. All of these will not be repeated here, but one will be discussed in some detail. The user must take heed of the fact that many of the states of NH_2 are strongly perturbed, which may result in significant effects on the intensities of transitions involving these levels. One must carefully ascertain that the transition(s) of interest does not involve perturbed levels. Much literature is available to examine for possible effects. We suggest some of the best sources to check are References 9-12.* A large number of Fermi (vibrational) type perturbations are known for this molecule (see, e.g., Reference 9). These apparently do not have any strong effect on the intensity of the $\tilde{A}$ $(0,N,0) \leftarrow \tilde{X}$ $(0,M,0)$ vibrational bands involving $\tilde{A}$ levels thus perturbed because, from perusal of the results of Mayama, et al.,[13] we find the lifetimes of the excited states have the expected magnitude. Since individual rotational states are not affected by this type of perturbation, one would not expect the HLFs to be changed either. Isolated rotational perturbations are therefore expected to cause the most trouble. These may generally be spotted readily, as for more symmetric molecules, by looking for unusual spin-splittings or for a rotational line appearing out of its expected place in a branch. As an example of the former, Dressler and Ramsay[9] give two figures showing examples of unusual spin-splittings in individual branches of two vibrational bands. The latter is not so easily spotted. For Σ vibronic levels a line appearing out of its expected place may be identified by using the approximation:

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*Since the original preparation of this manuscript, another paper of interest has appeared: S.C. Ross, F.W. Birss, M. Vervloet, and D.A. Ramsay, "The Absorption Spectrum of NH_2 in the Region 5300 to 6800Å," J. Mol. Spectrosc., Vol. 129, p. 436, 1988. This paper contains extensive discussion of perturbed levels as well as term values and constants which may be used to evaluate whether perturbations are present (see later).

$$T' \simeq \nu_0^K + B'[N(N+1) - K^2] - D'N^2(N+1)^2 \qquad (1)$$

where T' is the observed excited state term value, ν_0^K is the term value for N=0 in the excited state, B' and D' are the rotational constants, and N and K are the rotational quantum numbers. The difference of the two sides of this equation should be nearly zero if the level in question is not perturbed. The necessary constants are readily available from Table A1 of Jungen, Halpin and Merer's paper III[12] (JHM III). The observed term values may be obtained from Dressler and Ramsay.[9] Of course, the term values must be averaged over spin states. This procedure works well to confirm the perturbation which was pointed out by Dressler and Ramsay[9] at the 5_{05} level in $(0,9,0)\Sigma$. This state was also readily observed as perturbed because of its unusual spin-splitting.

For K>0 levels, Eq. 1 of JHM III may be used to predict unperturbed term values with a high degree of precision. These equations can be used to calculate positions of individual components of spin-orbit split and asymmetry-split levels. By comparing results with the observed term values, perturbed levels may be identified, even if unusual spin-orbit splittings are not clearly observed. For instance, Halpern, et al.,[14] observed an unusually long lifetime for the 4_{14} level of $(0,10,0)\Pi$, apparently after excitation of only the F_1 component. They suggested that this result is probably due to a perturbation, although none is immediately obvious from the spectra. There is no unusual spin-splitting for the level. (In fact, none is observed for any of the $N_{1,N}$ levels of this vibrational state.) Using Eq. 1 of JHM III, it is found that the predicted minus observed term value differences for this level are 0.97 and 0.66 cm^{-1} for F_1 and F_2 components, respectively. The 5_{15} level exhibits even larger differences, 1.22 and 0.80 cm^{-1} for F_1 and F_2, respectively. The quality of the fits are such that differences of less than about 0.5 cm^{-1} indicate significant perturbation is probably not present, 0.5-0.75 cm^{-1} is borderline, and greater than 0.75 cm^{-1} is perturbed. We therefore suspect both 4_{14} and 5_{15} are perturbed, the perturbation being stronger at 5_{15}. The nature of the perturber was not examined. This calculation supports Halpern, et al.'s, result. Unfortunately, they did not examine the F_2 spin state of 4_{14} or the 5_{15} states in their lifetime studies. It would clearly be of interest to do so.

In checking the literature for perturbed levels, the lifetime studies should also be examined.[13-15] As previously stated, unusually long lifetimes make one suspicious that a perturbation is present. Unfortunately, only a handful of the levels which exist have had lifetimes measured. Only one of these (see previous paragraph) exhibits a noticable effect on the lifetime. (I should note here that Mayama, et al.,[13] found from high resolution fluorescence exitation scans that the 1_{10} level of $(0,10,0)\Pi$ is also perturbed. Although this is the case, the perturbation is apparently not strong because the lifetime is not strongly affected). Though few levels have had measurements performed, lifetime results close to predictions would tend to indicate that a level is not perturbed. Such results indicate that calculated results using our method could be trusted. (For the method of prediction, see References 1 and 13. An example calculation is given in Section III A.)

Having made these observations about identifying perturbed states, the following notes are made regarding transitions for which we have published Einstein coefficients and/or oscillator strengths:[2,3]

A. $(0,11,0)\Sigma\ {}^{P}Q_{1,N}2$ & ${}^{P}Q_{1,N}3\ (2_{02} + 2_{12}$ & $3_{03} + 3_{13})$

Checks made using Eq. 1 indicate good agreement between predicted and observed values. Using an overlapped transition which simultaneously pumps 2_{02}, 3_{03}, and 4_{04}, the measured lifetime[14] is of the expected magnitude.[1,13] Therefore we believe no significant perturbation is present. Curiously, checks at N=5 and 6 of the $(0,11,0)\Sigma$ level indicate a borderline situation insofar as significant perturbation is concerned.

B. $(0,9,0)\Sigma\ {}^{P}Q_{1,N}7\ (7_{07} + 7_{17})$

The check using Eq. 1 again indicates good agreement of predicted and observed values. Halpern, et al.'s, measured lifetime[14] for the 7_{07} level, using a well-resolved excitation, agrees with the predicted magnitude[1,13] and is the same as lifetimes of other $N_{1,N}$ levels for this vibrational level. Therefore, we again believe no significant perturbation is present.

C. $(0,12,0)\Pi\ {}^{R}Q_{1,N}4\ (4_{14} + 4_{04})$

The observed and calculated 4_{14} term values differ by 0.660 cm^{-1}; thus, we have a borderline case. (Note: F_1 and F_2 components of all the $N_{1,N}$ observed states in this vibrational level are of the same value, that is, there is no observed spin-orbit splitting for this vibrational level.[9]) Agreement for $5_{1,5}$ is even worse, the difference being 1.31 cm^{-1}. A lifetime study[14] for $4_{1,4}$ yields the value 6.6 ± 1.1μs, which agrees fairly well with the value 5.0 ± 0.2μs found[13] for the 1_{10} level. Though these values do not quite overlap, the 4_{14} lifetime is well within error limits of the value one calculates using the VTMs from JHM II and the electronic transition moment (see References 1 and 13). This result indicates that perturbation, though perhaps present, is probably not significant to the oscillator strength calculation. We find this quite satisfying since our calculated oscillator strength agrees well with measured values.[3]

During our investigations of the $N_{1,N}$ and $N_{0,N}$ rotational states in the aforementioned vibrational levels, we found by comparing predicted and observed term values that the following states are probably perturbed significantly: 5_{15} in $(0,10,0)\Pi$; 5_{15} in $(0,12,0)\Pi$. These are in addition to those previously mentioned which are easily seen to be perturbed by unusual spin-splittings or lifetime measurements. It would clearly be of interest to perform lifetime measurements or other elucidating studies on these levels.

III. EXAMPLE CALCULATIONS

In addition to perturbations, there is one other problem pertinent to usage of the computer code to calculate HLFs for NH_2 of which the user should be aware. The program is written for a molecular transition which is asymmetric in both initial and final states. However, the upper state for the NH_2 $\tilde{A}$-$\tilde{X}$ transition is nearly linear. Proper correlation of upper states would have the molecule going through a near prolate symmetric top ($A > B = C$) conformation as the molecule approaches linearity. Of course, for the linear situation, one would have $A \to \infty$. However, this clearly cannot be handled

numerically. For our calculations, we used finite constants which fit the criterion A > B = C. This procedure, of course, cannot be used for the calculation of excited state energies, but the correct linestrengths are calculated. (Of course, the linestrengths do not depend on the values chosen.) Before leaving this subject, we should mention that the assumption that the upper state is a prolate symmetric top is acceptable for large values of v_2' since the molecule is approximately linear.[9] However, there is a small hump in the potential[16] which could affect this assumption for small values of v_2', that is, the molecule may not be close enough to linear for the prolate symmetric top approximation to work well. We have not investigated this possibility, but it would appear that levels above the first two or three vibrational quanta are probably sufficiently close to linear for the approximation to work well.

Having made these observations, we will now proceed with our example calculations. We note that the equation used to calculate Einstein coefficients for individual rotational lines is:[3]

$$A^{N'N''}_{v'v''} =$$

$$|\mu^0_e|^2(64\pi^4/3h)\langle v'|\sin(\rho/2)|v''\rangle^2\Delta\bar{\nu}^3_{v'v''}[S_{N'N''}/(2N'+1)] \quad . \qquad (2)$$

(Meanings of terms in this equation are discussed in Reference 3, Section II. Also note that the $A^{N'N''}_{v'v''}$ terms for $\Delta K_a = +1$ and $\Delta K_a = -1$ are averaged if $K_a' \neq 0$; see Discussion in Subsection C and in the last paragraph in Subsection A of this section.) We will discuss in the next three subsections the promised calculations of the $(0,11,0)\Sigma$ level lifetime and the A coefficients for the $^PQ_{1,N}7$ transition in the $(0,9,0)\Sigma - (0,0,0)$ band and $^RQ_{0,N}4$ transition in the $(0,12,0)\Pi - (0,0,0)$ band.

A. $\tilde{A}^2A_1$ $(0,11,0)\Sigma$ State Lifetime

We begin the calculation of the $(0,11,0)\Sigma$ lifetime by noting that the vibrational band coefficients, $A_{v'v''}$, are given by Eq. 2 without the normalized HLF term, i.e.:

$$A_{v'v''} = |\mu^0_e|^2(64\pi^4/3h)\langle v'|\sin(\rho/2)|v''\rangle^2\Delta\bar{\nu}^3_{v'v''} \quad . \qquad (3)$$

Two values are available for the electronic transition moment, μ^0_e (see references in Reference 3). We choose the measured value, $|\mu^0_e|^2 = (0.094 \pm 0.010)e^2a_0^2$, from Reference 8. The $e^2a_0^2$ term may take the uninitiated quite some time to determine. In cgs units, appropriate for spectroscopic calculations involving cm^{-1}, e is 4.8030×10^{-10} SC. (SC = statcoulombs, i.e., $dyne^{1/2}$-cm.) a_0 is the Bohr radius = 0.528Å. Thus, $64\pi^4e^2a_0^2/3h = 2.02 \times 10^{-6}$ cm^3/sec. The transition energy, $\Delta\bar{\nu}_{v'v''}$, may be estimated using the vibrational energy levels in Table 3 of JHM II. The vibronic transition moment, $\langle v'|\sin(\rho/2)|v''\rangle$, may be obtained from Table 7 of JHM II. It should be noted that JHM's notation for the levels in these tables is given in the bent molecule notation. Linear notation is used for the excited state of this molecule by most authors. The equation relating linear and bent notations is:

$$v_{linear} = 2v_{bent} + \ell \qquad (4)$$

where ℓ (the vibronic angular momentum) is taken to be $K_a + 1$. Thus, for the $(0,11,0)\Sigma$ state, we have $K_a = 0$ and $v_{bent} = 5$. From Table 3 of JHM II we therefore find for the $\tilde{A}$ $(0,11,0)\Sigma$ state an energy, E', of 18483.98 cm^{-1}. For the ground state levels, we must have $K_a = 1$ since $\Delta K_a = \pm 1, \pm 3, \pm 5 \ldots$ ($|\Delta K_a| > 1$ transitions are ignored for this calculation since they are weak.) For the (0,0,0) $K_a = 1$ level, for example, JHM give an energy, E" = 23.58 cm^{-1}. (Of course, only the first three digits in the difference of these energies have much significance to our calculation so that the rotational energies of particular transitions may be ignored.) Now, to determine the excited state lifetime, we must sum over $A_{v'v"}$ values since $\tau^{-1} = \Sigma_{v"} A_{v'v"}$. Thus,

$$\tau^{-1} = |\mu_e^0|^2 (64\pi^4/3h) \Sigma_{v"} \langle v' | \sin(\rho/2) | v" \rangle^2 \Delta E^3 \qquad (5)$$

where $\Delta E = E' - E" = \Delta\bar{\nu}_{v'v"}$. The numerical results for terms in the summation of Eq. 5 are given in Table 1. The total of these terms is

$$\Sigma_{v"} \langle v' | \sin(\rho/2) | v" \rangle^2 \Delta E^3 = 8.371 \times 10^{11} \text{ cm}^{-3} .$$

(It is interesting to note that only the first 5 to 7 terms in the summation have much effect on the total emission; see Table 1. This result occurs because the ΔE^3 term becomes quite small, that is, the longer wavelength emissions which occur to the higher ground state vibrational levels do not have as high a probability as short wavelength emissions, as one would expect.) Thus, we find $\tau^{-1} = 1.59 \times 10^5$ sec^{-1} and $\tau = 6.3 \mu s$. (Using the calculated value $\mu_e^0 = 0.10 e^2 a_0^2$ chosen by JHM,[1] we find $\tau^{-1} = 1.69 \times 10^5$ sec^{-1} and $\tau = 5.9$ μs, in perfect agreement with their results as it should be; see JHM II, Table 10.)

Before leaving this discussion of the lifetimes calculation, we should note that one additional factor must be considered if $K_a' \neq 0$. (See JHM II, p. 55.) There is an additional factor of 1/2 for emissions having $\Delta K_a = +1$ and $\Delta K_a = -1$ in this case. That is, the two terms for each vibrational band, one having $K_a" = K_a' + 1$, the other $K_a" = K_a' - 1$, must be averaged in forming the sum of Eq. 5. This averaging of two terms must also be included in Eqs. 2 and 3 if $K_a' \neq 0$.

B. Transition Strength of $(0,9,0)\Sigma - (0,0,0)$ $^PQ_{1,N}7$

We next consider the calculation of transition strength for the $^PQ_{1,N}7$ in the $(0,9,0)\Sigma - (0,0,0)$ band. From Table 3 of JHM II, we find E' - E" = 16752.80 - 23.58 = 16729 cm^{-1}. The VTM from Table 7 of JHM III is -0.3020. Using the measured[13] μ_e^0, we find $A_{v'v"} = 8.11 \times 10^4$ sec^{-1}. Application of the program to calculate HLFs yields $S_{N'N"} = 6.7638$ for a $^PQ_{1,N}7$ transition ($7_{07} \leftarrow 7_{17}$). Thus, $S_{N'N"}/(2N'+1) = 0.451$ and $A_{v'v"}^{N'N"} = 3.66 \times 10^4$ sec^{-1} for this transition. Using the well-known relation

$$f = (mc/8\pi^2 e^2)(g_2/g_1)\lambda_0^2 A_{21} = (1.50 \text{ cm}^{-2} \text{ sec})(g_2/g_1)\lambda_0^2 A_{21} \qquad (6)$$

we may very simply find the oscillator strength for this transition. From Dressler and Ramsay,[9] the transition wavelength, in vacuum, is $\lambda_0 = 5973.8$Å.

Since we are dealing with a Q branch transition, $N' = N'' = 7$ and $g_1 = g_2 = 15$. Thus, we find $f = 1.96 \times 10^{-4}$ for the transition.

Table 1. Example Calculation of Terms in the Summation Involved in the Calculation of an NH_2 Excited State Lifetime. The example is for the $(0,11,0)\Sigma$ state of $\tilde{A}^2A_1$. (This is the $(0,5,0)$ $K_a = 0$ level in the bent molecule notation used by JHM.)

v"	$E_{v''}$ (cm^{-1})	ΔE (cm^{-1})	$\langle v' \lvert \sin(\rho/2) \rvert v'' \rangle$	$\Delta E^3 \langle v' \lvert \sin(\rho/2) \rvert v'' \rangle^2$ (cm^{-3})
0	24	18,460	0.2934	5.415×10^{11}
1	1,521	16,963	0.1318	8.479×10^{10}
2	2,987	15,497	-0.1823	1.237×10^{11}
3	4,422	14,062	0.0618	1.062×10^{10}
4	5,822	12,662	-0.1618	5.315×10^{10}
5	7,185	11,299	0.0154	3.421×10^{8}
6	8,504	9,980	0.1257	1.571×10^{10}
7	9,761	8,723	0.0673	3.006×10^{9}
8	10,859	7,625	-0.0785	2.732×10^{9}
9	11,845	6,639	0.0464	6.300×10^{8}
10	12,987	5,497	-0.0521	4.509×10^{8}
11	14,044	4,440	-0.0686	4.119×10^{8}
12	15,449	3,035	0.0157	6.891×10^{6}

C. Transition Strength of $(0,12,0)\Pi - (0,0,0)$ $^RQ_{0,N}4$

Finally, we consider the strength of the $^RQ_{0,N}4$ transition in the $(0,12,0)\Pi - (0,0,0)$ band. This is done to give an explicit example of the averaging of terms for the two different $A_{v',v''}$ values which result for the two possible ΔK_a's, as discussed earlier in this section. For $\Delta K_a = +1$ ($K_a' = 1$, $K_a'' = 0$), we find from JHM II, Table 3 that $E' - E'' = 19349.54 - 0 = 19349\ cm^{-1}$, and from Table 7, the VTM is -0.2692. This leads to $A_{v',v''}(\Delta K_a = +1) = 9.972 \times 10^4\ sec^{-1}$. For $\Delta K_a = -1$ ($K_a' = 1$, $K_a'' = 2$), we similarly find $E' - E'' = 19349.54 - 94.10 = 19255\ cm^{-1}$ and the VTM is -0.2721. This leads to $A_{v',v''}(\Delta K_a = -1) = 10.037 \times 10^4\ sec^{-1}$. Averaging these two terms (as directed in JHM II, p. 55), we find $A_{v',v''} = (9.972 \times 10^4 + 10.037 \times 10^4)/2 = 1.00 \times 10^5\ sec^{-1}$ for the $(0,12,0)\Pi - (0,0,0)$ band. From the program, the HLF for an

$^{R}Q_{0,N}4$ transition ($4_{14} \leftarrow 4_{04}$) is $S_{N'N''} = 6.3806$. Thus, $S_{N'N''}/(2N'+1) = 0.709$ and $A_{v'v''} = 7.09 \times 10^{4}$ sec^{-1} for the transition of interest. Using Eq. (6), and $\lambda_0 = 5167.6$Å (vacuum) from Dressler and Ramsay,[9] we find $f = 2.84 \times 10^{-4}$ for the transition.

IV. CONCLUSION

In this monograph we have provided example calculations of NH_2 lifetimes, Einstein coefficients and oscillator strengths. The reader is cautioned to thoroughly read Section II of Reference 3 and take heed of the caveats mentioned therein. In particular, we warn that the calculation may not work well for transitions involving perturbed levels. Simple methods of determining whether a level is perturbed were discussed here. It is hoped that this monograph will make application of our calculational method easier for the uninitiated.

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